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BIOLOGICAL ACTION OF TOLUENE DIISOCYANATE AND METHYLENEDIANILINE IN WATER (FINAL REPORT)

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TRANSLATION

Spargnapani Translation Bureau Ltd.
DALTON ENTRY NEW CHURCH HOUSE
34 JOHN DALTON STREET MANCHESTER M2 6LE
Telephone: 061-834 7431/2

BIOLOGICAL ACTION OF TDI AND MDI IN WATER

TABLE OF CONTENTS

1 - INTRODUCTION

The problem concerned is to investigate the impact of an accidental spill of TDI or MDI on an aquatic system *.

The aim of this study is restricted to investigating the toxicity of isocyanates in terms of certain organisms chosen as samples among fish, crustaceous species, molluscs and seaweed, and to measuring their biodegradability in the presence of a bacterial flora.

It is well known that with the water of a natural aquatic medium, isocyanates react to give insoluble polyureas and, in a transitory state, small quantities of soluble amines which may of course play an important part in the toxicity of the medium. We noticed that after a 24-hour contact, the quantity of amines formed seemed to depend on the natural reconstituted medium specially prepared for each organism. For instance:

With the medium fish	Starting solution 500 mg/1 of	
	TDI	MDI
	10 mg/1 of TDA formed	4 mg/1 of MDA formed
Medium bacteria	Starting solution of	
	TDI	MDI
	100 1000	100 mg/1
	20 28	
Distilled water	Starting solution of 100 mg/1	
	TDI	
	15 mg/1 of TDA	2mg/1 of MDA

* Cf. Technical annex to contract

This observation led us to consider not only the harmful effects brought about by the isocyanates themselves, but also by their respective amines.

2 - CONCLUSION

Starting from TDI or MDI, after a 24-hour contact in a given aqueous medium, the concentration in corresponding amines formed seems constant (2 to 25 ppm). This range of concentrations is located below the toxic limits.

For each of the groups studied (fish, molluscs, crustaceous species, seaweed) the following results were noted:

2.1 Isocyanates

Fish, crustaceous species, molluscs

For raw MDI, pure MDI and TDI the noxious limits are far above 500 mg/1.

Seaweed

The same conclusion is valid for seaweed, except for synecocystis which appears to be more sensitive.

2.2 Amines

	MDA	TDA
Fish		
LC 50 24 hrs. mg/1	48	260
Crustaceous species	66	64
Molluscs		
Embryos	220	220
Young ones	210	175
Seaweed		
Chlorilla	$1 < S < 10$	$10 < S < 100$
Nietzschia	$10 < S < 100$	$1 < S < 10$
Synechocystis	$1 < S < 10$	$0.1 < S < 1$

NIOSH distinguishes the products of

class 0	TLm concentration >	1000 mg/1 - insignificant hazard
class 1		100 - 1000 mg/1 - practically non-toxic
class 2		10 - 100 mg/1 - slightly toxic
class 3		1 - 10 mg/1 - moderately toxic
class 4		< 1 mg/1 - highly toxic

2.3 Notes

On crustaceous species and molluscs, MDA and TDA have a similar toxicity.

On the other hand, MDA is more toxic than TDA where fish are concerned.

Seaweed appears sensitive to these amines, a greater sensitivity of synechocystis being noted.

The biodegradability for TDA is small and that for MDA medium (average) over 42 days, but with a flora not specially adapted.

These results may be useful for the manufacture or use of amines.

3 - EXPERIMENTAL RESULTS

3.1 Seaweed

3.1.1 Principle

Introduce the substance to be tested into the nutrient medium for the species considered. Inoculate via a small number of cells. Incubate in conditions favourable to growth. Read the importance (extent) of the development in relation to a control at the moment the latter has multiplied sufficiently.

3.1.2 Introduction of the isocyanates

This is effected by the intermediary of pentane for Desmodur T 80 (TDI). As MDI is not soluble in this solvent, it has not been studied.

3.1.3 Results

1) Technical isocyanate, pentane *

	CHLORELLA pyrenoidosa (3 tests)	NIETZSCHIA frustulum (3 tests)	SYNECHOCYSTIS cedorum (3 tests)
Desmodur T80 (TDI)	$S > 100$ mg/1	100 mg/1 $<$ $S < 1000$ mg/1	$S < 1$ mg/1

2) Amines

Amine	CHLORELLA pyrenoidosa (3 tests)	NIETZSCHIA frustulum (3 tests)	SYNECHOCYSTIS cedorum (1 test)
MDA	1 mg/1 $<$ $S < 10$ mg/1	10 mg/1 $<$ $S < 100$ mg/1	1 mg/1 $<$ $S < 10$ mg/1

* This solvent was used to allow greater precision in the dilutions. Its complete disappearance from the test medium was controlled.

3.2 On molluscs

3.2.1 Organism - Limnea stagnalis

Age 6 to 8 days (eggs laying)

1 to 4 days (young)

3.2.2 Method

3.2.2.1 Conditions of experiment:

20°C ± 1°C darkness

3.2.2.2 Dilution water - ph. 8.0 ± 0.2

(reconstituted river water)

$NaHCo_3$ - 0.200 g

$CaCl_2$ - 0.224 g

K_2SO_4 - 0.026 g

Water q.s.p. - 1000 ml.

Dissolved oxygen > 80% of saturation

3.2.2.3 Number of animals:

For each concentration (100 cc): 2 to 3 layings

(i.e. several hundred eggs) and 25 grown ups.

3.2.2.4 Observation with binocular lens

Lack of motion was noted

3.2.2.5 Determination of the Ci (LC) 50 on log probit paper

(concentration determining the lack of motion) of 50%

of the animals.

3.2.3 Preparation of substances

See preparation (tests on fish) using reconstituted river water.

3.2.3.1 Isocyanates:

The substance is dispersed in the reconstituted river water by magnetic stirring for 18 hours.

The preparation obtained is very heterogenous; a large part of the substance precipitates and clusters at the bottom of the vessel or gathers on the surface.

The daphnies are introduced into the preparation as it is, without elimination of the insoluble portion.

3.2.3.2 Amines:

The substances are dissolved in the reconstituted river water by magnetic stirring for 18 hours.

Mother liquours were prepared at the following concentrations:

TDA: weighment of 500 mg for 1 litre

MDA: weighment of 500 mg for 1 litre

3.2.4 Results

3.2.4.1 Isocyanates

MDI monomer

Concentration in mg/l	Eggs mortality of embryos in %	Young ones mortality in %	
500	0	0	LC_{50} - 24 hours $\gg$ 500mg/l.
Control reconstituted river water	0	0	

Desmodur 44 V 20

Concentration in mg/l	Eggs mortality of embryos in %	Young ones mortality in %	
500	0	0	LC_{50} - 24 hours $\gg$ 500mg/l
Control reconstituted river water	0	0	

Desmodur T 80

Concentration in mg/l	Eggs mortality of embryos in %	Young ones mortality in %
500	0	0
Control reconstituted river water	0	0

LC_{50} - 24 hours >> 500 mg/l

3.2.4.2 Amines:

MDA

Concentrations in mg/l	Eggs mortality in %	Young ones mortality in %
500	100	100
320	100	100
200	30	45
120	0	0
80	0	0
50	0	0

LC 50 - 24 hours: 220 mg/l for the eggs
210 mg/l forthe young ones

TDA

Concentrations in mg/l	Eggs mortality in %	Young ones mortality in %
500	100	100
320	90	100
200	40	70
120	[illegible]	5
80	0	0
50	0	0

LC 50 - 24 hours: 220 mg/l for the eggs
175 mg/l forthe young ones

3.3 On crustaceous species

3.3.1 Organism Daphnia magna strauss

age: from 24 to 72 hours

3.3.2 Method

Norma AFNOR-T. 90.301 April 1974 (French Standard)

3.3.2.1 Test conditions:

20°C ± 1 darkness

3.3.2.2 Dilution water: pH 8.0 ± 0.2

See tests - molluscs

dissolved oxygen more than 80% of saturation

3.3.2.3 Number of animals:

for each concentration (10cc) 5 daphnies, four repetitions.

3.3.2.4 Visual observation:

lack of motion noted

3.3.2.5 Determination of the LC 50 on log probit paper

3.3.3 Preparation of products

Dilution in the reconstituted river water (molluscs)

3.3.3.1 Isocyanates

The substance is dispersed in the reconstituted river water by magnetic stirring for 18 hours.

The preparation obtained is very heterogenous; a large part of the substance precipitates and clusters (polyurea) at the bottom of the vessel or comes together on the surface.

The daphnies are introduced into the preparation as it is, without elimination of the insoluble part (We did not want to remove substances capable of having some solubility).

3.3.3.2 Amines:

The substances are dissolved in the reconstituted river water by magnetic stirring for 18 hours.

Mother liquors were prepared at the following concentrations:

TDA = weighment of 500 mg for 1 litre

MDA = weighment of 500 mg for 1 litre

3.3.4 Results

3.3.4.1 Isocyanates

MDI monomer

Concentration of isocyanate in mg/l	Mortality in%
500	0
Control reconstituted water	0

LC 50 - 24 hours >> 500 mg°/1

Desmodur 44 V 20

Concentration of isocyanate in mg/l	Mortality in %
500	0
Control reconstituted water	0

LC 50 - 24 hours >> 500 mg/1

Desmodur T 80

Concentration of isocyanate in mg/l	Mortality in %
500	0
Control reconstituted water	0

LC 50 - 24 hours >> 500 mg/1

* We think that the introduction of 500 mg/l into the environment is a strong concentration.

3.3.4.2 Amines

MDA

Concentrations in mg/l	Mortality in 24 hours (5 tests on 5 daphnies in 10 cc)	Mortality in %
50	1/5 2/5 3/5 1/5	35
70	2/5 2/5 3/5 2/5	45
90	4/5 4/5 4/5 2/5	70
120	5/5 5/5 5/5 4/5	95
170	5/5 5/5 5/5 5/5	100

LC 50 - 24 = 66 mg/l

Confidence limits (intervals) 55-75 at probability 95%.

TDA

Concentrations in mg/l	Mortality in 24 hours (5 tests on 5 daphnies in 10 cc)	Mortality in%
50	1/5 1/5 2/5 2/5	30
70	3/5 2/5 2/5 3/5	50
90	3/5 5/5 4/5 5/5	80
120	5/5 5/5 5/5 5/5	100
170	5/5 5/5 5/5 5/5	100
Control reconstituted water	0/5 0/5 0/5 0/5	0

LC 50 - 24 hours = 64 mg/l

Confidence intervals 55 - 72 at probability 95%

3.4 On fish

3.4.1 Organism Brachydano rerio, 3 ± 0.5 cm long, growth at 26°C.

3.4.2 Method

AFNOR draft standard, proposition no.3 of November 1976 (ref. T.95.C. doc. 17). "Determination of the acute toxic effects of a substance on fish. Static test".

3.4.2.1 Test conditions : 20°C + 1

Day light + fluorescent tubes

Light 8 hr/day

3.4.2.2 Acclimatization of the animals.

At the test conditions 8 days before use.

Not fed 24 hours before start of the experiment.

3.4.2.3 Dilution water

(reconstituted river water)

Its characteristics are:

pH 7.8 + 0.2

hardness 100 mg/l expressed in calcium carbonate,

dissolved oxygen > 90% of saturation.

100 litres of this water contain:

- 50 ml of solution 1	($CaCl_2$ 6 H_2O	320 g
	(Na Cl	29 g
	(Na NO_2	9 g
	(water q.s.p.	1 litre
- 50 ml of solution 2	(Mg SO_4 7 H_2O	151 g
	(Na_2 SO_4	79 g
	(water q.s.p.	1 litre
- 50 ml of solution 3	(Na H CO_3	29 g
	(water q.s.p.	1 litre

3.4.2.4 Number of fish:

5 fishes are used for 1 litre of preparation. The test is repeated 4 times for each concentration.

3.4.2.5 Expression of the results:

Calculation of the LC 50 (lethal concentration for 50% of the animals). We also observed the behaviour of the animals during the test.

3.4.3 Preparation of substances in the water

3.4.3.1 Isocyanates

The substance is dispersed in the reconstituted river water by magnetic stirring for 18 hours.

The preparation obtained is very heterogenous; a large part of the substance precipitates and clusters at the bottom of the vessel or comes together on the surface (polyurea).

The fishes are introduced into the preparation as it is, without elimination of the insoluble part.

A concentration of amine in the water is effected at the end of test, after filtration to 0.2µ on membrane.

The following quantities were found:

MDA (concentration 375 nm)

500 mg of MDI monomer (pure MDI) for 1 litre → 4 mg/l MDA

500 mg of Desmodur 44 V 20 (polymeric MDI)

for 1 litre ---→ 3.5 mg/l of MDA

TDA (concentration 460 nm)

500 mg of Desmodur T 80 (TDI) for 1 litre --→ 10 mg/l of TDA

3.4.3.2 Amines:

The substances are dissolved in the reconstituted river water by magnetic stirring for 18 hours.

Mother liquors were thus prepared at the following concentrations:

TDA - weighment of 2680 mg for 1 litre

MDA - weighment of 500 mg for 1 litre

3.4.4 Results

3.4.4.1 Isocyanates

MDI monomer (pure MDI)

Concentration of isocyanate in mg/l	Concentration of MDA in the preparation (solution) in mg/l	Mortality in 24 hours %
500	4	0
Control reconstituted water	-	0

LC 50 - 24 hours $>>$ 500 mg/l

Desmodur 44 V 20 (Polymeric MDI)

Concentration of isocyanate in mg/l	Concentration of MDA in the solution in mg/l	Mortality in 24 hours %
500	3.5	0
Control reconstituted water	-	0

LC 50 - - 24 hours $>>$ 500 mg/l

Desmodur T 80 (TDI)

Concentration in isocyanate in mg/l	Concentration of TDA in the solution in mg/l	Mortality in 24 hours %
500	10	0
Control reconstituted water	-	0

LC 50 - 24 hours $>>$ 500 mg/l

3.4.4.2 Amines

MDA

Concentrations in mg/l	Mortality in 24 hours (5 tests on 5 fishes in 1 l.)				Mortality in %
40	0/5	0/5	0/5	0/5	0
50	2/5	3/5	4/5	5/5	70
65	5/5	5/5	5/5	5/5	100
85	5/5	5/5	5/5	5/5	100
Control reconstituted water	0/5	0/5	0/5	0/5	0

LC 50 - 24 hours = 48 mg/l

Confidence intervals 45 - 51 at probability 95%

TDA

Concentrations in mg/l	Mortality in 24 hours (5 tests on 5 fish in 1 l.)				Mortality in %
150	0/5	0/5	0/5	0/5	0
200	0/5	1/5	0/5	0/5	5
250	0/5	0/5	2/5	1/5	15
320	5/5	5/5	5/5	5/5	100
420	5/5	5/5	5/5	5/5	100
Control reconstituted water	0/5	0/5	0/5	0/5	100

LC 50 - 24 hours = 260 mg/l

Confidence intervals 254 - 289 at probability 95%

4 - MATHEMATICAL STUDY OF THE ECOTOXICITY OF AMINES DERIVED FROM ISOCYANATES MDI AND TDI

Introduction

For each concentration of a substance, observations are carried out on four tanks containing 5 fishes.

The substances submitted to examination are:

1) TDA at concentrations (expressed in mg per litre)

D1	D2	D3	D4	D5	D6
0	150	200	250	320	420

The observations are carried out at times t_1 = 18 hours and t_2 = 24 hours.

i.e. in total 4 repetitions x 6 concentrations x 2 times = 48 observations for the TDA.

2) MDA at concentrations (expressed in mg per litre)

D1	D2	D3	D4	D5
0	40	50	65	85

The observations are carried out at times t_1 = 25 minutes t_2 = 1 hr. t_3 = 3 hrs. t_4 = 24 hrs.

i.e. in total 4 repetitions x 5 concentrations x 4 times = 80 observations for the MDA.

The observations consist of noting the symptoms observed on each fish. As the repetitions comprise 5 fishes, the result will have the form:

Symptom X = 2 Symptom Y = 3

Nature of the observations (symptoms)

Code machine	Description of symptom
A 001 or A	. normal swimming
A 002 or B	. slow swimming
A 003 or C	. motionless in normal position at the bottom
A 004 or D	. motionless in normal position at surface
A 005 or E	. motionless at surface with head upward
A 006 or F	. disequilibrium in the solution
A 007 or G	. disequilibrium at surface
A 008 or H	. disequilibrium at the bottom
A 009 or I	. death

4.1 Method used for mathematical analysis

We obtain a table of 128 lines (observations) and 9 columns (symptoms). The factorial analysis of the relations goes through a series of graphic representation to enable studying the relationships,

a) between symptoms

b) between observations (effect concentration-substance-time)

c) between observations and symptoms (classification of the concentration effects, substance effects, time effects).

We do not lay stress on the mathematical study itself, we have merely drawn from a listing of 18000 lines of data which concerns the practitioner and we have interpreted by means of the various results provided by the computer.

The procedure is as follows: a very approximate plan of several symptoms is evolved; all the observations thus located in this plan could be classified in relation to these symptoms; as many

plans as necessary are evolved to gather all the data contained in the tests.

4.2 Results obtained

A) STUDY OF THE SYMPTOMS

This is summarized in 5 very simple graphs enclosed.

In GRAPH series 1 symptoms, we find:

GRAPH 1 (axes 1 and 2)

the symptoms points [A] [B] [I]

As in all the following graphs, only the squared points [ ] are to be studied in the proposed GRAPH.

The relationship with [A] will indicate for the individuals the fish identical to the control, the relationship with [B] will indicate a very small toxic concentration or simply variation of a purely biological order which will be corrected by the repetitions.

The relationship of an observation with [I] will indicate the clear effect of a toxic substance.

In GRAPH 2 of the same series there will be the same type of classification except that the death [I] is replaced by the symptom [H] (disequilibrium at the bottom).

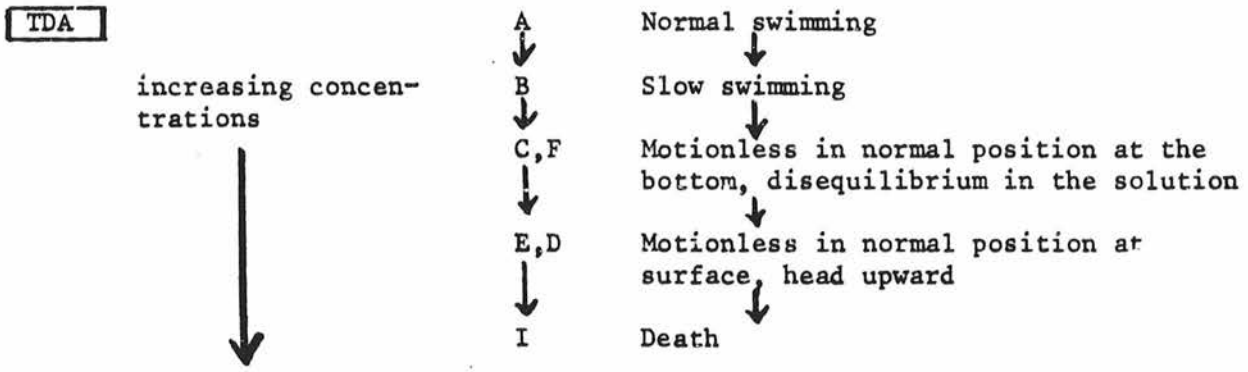
But one realizes immediately that a classification, in relation to graded physiological states, will enable awareness of the cumulative toxic effects of pollutants present in the medium in a sporadic way and still very much below the CL 50.

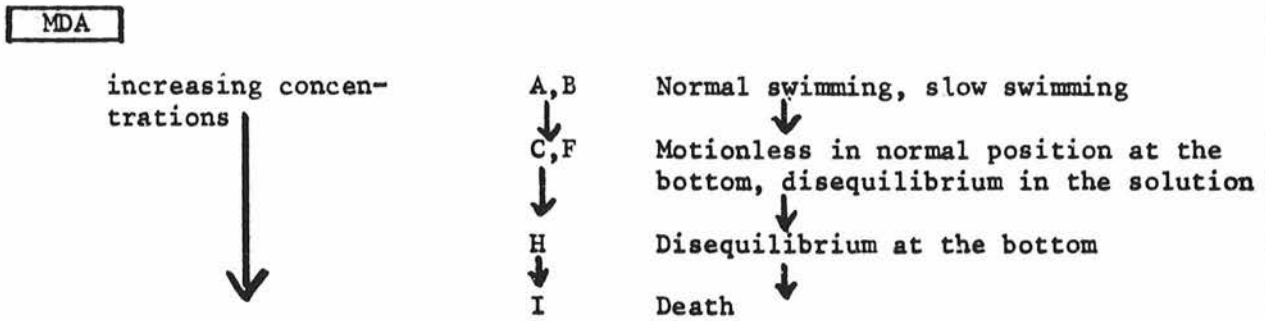
Likewise in the following series we have:

GRAPH 3	A	normal swimming
	F	disequilibrium in the solution
GRAPH 4	I	death
	H	disequilibrium at the bottom
GRAPH 5	I	death
	F	disequilibrium in the solution

B) HIERARCHY OF THE SYMPTOMS

according to the Substance - concentration effect





C) STUDY OF THE OBSERVATIONS -

EFFECTS TIME - CONCENTRATION - SUBSTANCE

1) Diagram of GRAPH 1 of the symptoms (Axes 1,2)

On GRAPH, series 4, will be found side by side the symptoms characterizing the diagram, i.e. A, B, I.

The relationship with A009 = I in the small graphs gives the approximate LC 100 at each observation period and for each substance.

To simplify the GRAPH, the mean of the four repetitions for each substance concentration has been carried over because they are very coherent. The code is interpreted in the following manner:

1 MD 4

means the MDA observation time, concentration no.4.

the 1st figure indicates the observation time

the 1st letter designates the substance

the last two characters: the concentration

TDA at time t = 18 hrs. all the fish are dead for concentration 6 at time t = 2 hrs. for concentration 5.

MDA at time t = 25' no deaths

at time t = 7 hrs. lethal concentration = D5

at time t = 3 hrs. lethal concentration = D5

at time t = 24 hrs. lethal concentration = D4

In another connection it should be noted that the controls are located close to A001, normal swimming, and the small concentrations close to A002, slow swimming.

2) DIAGRAM OF GRAPH 2 of the SYMPTOMS (Axes 1,3)

The upper part of this diagram shows clearly the intermediate transition, via symptom A001 = H = disequilibrium at the bottom, of the D2 concentrations of MDA at time t = 25 minutes, the D3 and D4 concentrations of MDA at time t = 1 hr.

4.7 - CONCLUSION

The analysis of the data enables coding of the qualitative observations (symptoms) and processing the tables of numbers thus obtained; it synthesizes the results in the form of charts (cards) which display the phenomenon visually. It can thus process notes attributed to phenomena.

In the subject dealt with here the important point is, that as in the case of many other examples in ECOTOXICOLOGY, the observations and measurements carried out before the death of the animal are much more abundant in education (information ?) than the CL_{50}, particularly in the case of relatively small sporadic pollutions or repeated absorption of small concentrations of a pollutant.

The fact of seeing 50 mg of MDA create in one hour symptoms of last degree seriousness before death is important information
The fact of being able to establish a hierarchy of the symptoms also seems to us very useful.

5 - ANNEXES

5.1 BIODEGRADABILITY

5.1.1 Preliminary tests

This study was necessary in order to make it possible for us to know the non-toxic concentrations in our studies of biodegradability.

5.1.1.1 Method

1) Substances examined

TDA

TDI

2) Principle

To submit bacteria from urban waste waters to the action of the substances for 24 hours. Then count the surviving mesophilic aerobic bacteria. Compare with a control (annexe 5.5)

5.1.1.2 Preparation of the substances

2.1 TDI - We estimate the preparations (solutions) of TDI by the TDA which it produces in an aqueous medium.

Preliminary tests show that an acetonic solution of TDI at 100 g/l:

diluted 100 times in the "biodegradability" medium gives 28 mg/l of TDA in 24 hours

diluted 1000 times in the "biodegradability" medium gives 19 mg/l of TDA in 24 hours.

We adjust this first dilution to 20 mg/l of TDA (contributed by the TDI) and prepare solutions to 10, 1, 0.1 mg/l.

(Before concentrating the TDA, filtering is carried out to eliminate the insoluble part which is formed when we dilute the acetonic solution of TDI in the aqueous medium) mixing carried out by means of sonication (Bransonic 220 50 Hz 125 W - 5 minutes).

2.2 TDA mother liquor at 1 g/l in the medium used for the biodegradability tests (AFNOR T.95-D-doc 18 - Eaux biodégradabilité). Then dilutions to obtain concentrations of 100, 50, 20, 10, 1, 0.1 mg/l.

5.1.1.3 Preparation of bacteria

Bacteria from the water entering the purification plant of St-Germain au Mont d'Or. Bacteria washed, concentrated and put back into suspension in the "Ringer". The inoculum thus prepared at an adsorption of 0.415 to 620 nm. 1 ml is used for 100 ml of solution of substance.

5.1.1.4 Incubation

24 hours with shaking (backward and forward motion) at 25°C.

5.1.1.5 Results

Substances		Bacteria per ml
Control		4.1×10^6
Pure TDA	100 mg/l	3.8×10^6
	50 "	9.0×10^6
	20 "	5.5×10^6
	10 "	5.8×10^6
	1 "	5.6×10^6
	0.1 "	3.2×10^6
TDA from TDI	20 mg/l	7.5×10^6
	10 mg/l	7.4×10^6
	1 mg/l	4.3×10^6
	0.1 mg/l	3.2×10^6

5.1.1.6 Conclusions

At the tested concentrations, TDA either pure or obtained from TDI had no effect on the number of bacteria from urban waste waters. Biodegradability assays are to be considered. However, the above results do not imply that there is no inhibiting effect of the TDA on the bacterial metabolism.

Note:

This assay was not performed on the MDI and MDA.

5.1.2 Main tests

5.1.2.1 Organisms

Mainly bacterial in urban waste waters.

5.1.2.2 Method

Draft AFNOR T.95 D doc. 18, 1976

5.1.2.2.1 Test conditions: 25°C ± 1

in darkness

5.1.2.2.2 Principle

The evolution of biological degradability has been followed by concentration of the dissolved organic carbon occassioned by the molecule. The concentrations were carried out on Beckman Analyser 915A after centrifuging the samples (3ml), 15 minutes at 5000 g .

For each flask the contents in organic carbon were calculated by the difference between total carbon - inorganic carbon; the reference curves used varied from 1 to 25 ppm for the inorganic carbon and from 1 to 25 or 10 to 100 ppm according to the case, for the total carbon; the concentrations of each flask were calculated on computer on the basis of these curves.

5.1.2.3 Preparations of substances and inoculum

The substances put in solution in a water at pH 7.5 containing macro and micro elements, were constantly shaken in 500 cc Erlenmeyer flasks and inoculated with a bacterial inoculum prepared from urban waste waters at a concentration of 5 ± 3.10^7/ml. Each test was repeated three times (flasks 1-2-3).

5.1.2.4 Conclusion:

The amount of biodegradation for toluylene diamine is of the order of 12% in the test conditions.

Diphenyl methane diamine is liable to be biodegraded at values approaching 53%.

Translator's note

Please note that I have not translated tables P25 and 26 of the original as the headings and comments have already been translated and/or amended on the corresponding tables in the document lent for guidance.

5.2 SUBSTANCES STUDIED

5.2.1 T D I (Desmodur T.80)

Toluylene diisocyanate

Percentage purety: 99.99

Mixing of two isomers:

- 80% 2.4 toluylene diisocyanate
- 20% 2.6 " "

5.2.2 MDI

4.4' Pure diphenyl methane diisocyanate

5.2.3 Polymeric MDI (Desmodur 44 V 20)

5.2.4 TDA: Toluylene diamine

Mixture of two isomers (corresponding to the starting isocyanate)

5.2.5 MDA: diamine corresponding to the polymeric MDI

5.3

SC/EE - 13 - ISOCYANATE/AQUATIC LIFE

RESEARCH PROPOSAL

I - AIM

Try to determine the eventual risks on the environment when TDI/MDI are accidentally spilled near or in rivers.

II - RESEARCH PROJECT

In a first step, the project will include only short term studies.

II-1) Microorganisms

Tests on 3 species of algae:

- Chlorella;
- Nitzchia;
- Synecoccus.

II-2) Snails

Tests on Limnea stagnalis (AFNOR projected standard test).

II-3) Crustaceous species

Test on Daphnia magna (AFNOR standard test)

II-4) Fishes

- Small trout (Salmo) (EPA standard test): probably Salmo Fario
- Or Zebra fish (ISO projected standard test).

II-5) Biodegradability (AFNOR projected standard test).

Carbon determination

II-6) Determinatic of aromatic amines (if any)

III- DURATION AND COST OF PROJECT

Expected delay for answer: 3 to 4 months.

Cost: $6 000.

J. MOCOTTE
RHONE-POULENC
Water Research Laboratory
DECINES 69 - FRANCE

5.4 METHODS OF ANALYSIS

TDA concentration

To 100 ml of water add: 25 ml of buffer pH3 (potassium phtalate acid 10.2 g - HCl 0.1 N 203 ml in one litre of water)
and 1 ml of nitrazol (4%)
Leave 5 minutes in darkness

MDA concentration

To 100 ml of water add:
25 ml of buffer pH9 (boric acid 0.1 M 500 ml - NaOH o.1 N 213 ml in one litre of water)
and 1 ml of nitrazol (4%)
Leave 5 minutes in darkness

The measurements were carried out on a Varian spectrophotometer at 460 nm (TDA) and 375 nm (MDA)

5.5 COMPOSITION OF THE MEDIUM USED FOR BIODECREDATION

1 ml of microelements solution for 1 litre of macroelements solution

Microelements solution	mg	Macroelements solution	g
$Fe\ SO_4,\ 7\ H_2O$	100	$(NH_4)_2\ SO_4$	0.30
$Mn\ SO_4,\ H_2O$	100	$NH_4\ NO_3$	0.15
$K_2Mo\ O_4$	25	$KH_2\ PO_4$	0.30
$Na_2\ B_4\ O_7\ ,\ 10H_2O$	25	$Na_2\ HPO_4,\ 12H_2O$	2.00
$CO(NO_3)_2\ ,\ 6H_2O$	25	$Mg\ SO_4,\ 7\ H_2O$	0.05
$Cu\ Cl_2,\ 2\ H_2O$	25	$Ca\ Cl_2$	0.05
$Zn\ Cl_2$	25	Bacto-autolyzed yeast	0.005
$NH_4\ VO_3$	10	Distilled water q.s.p.	1 l
Distilled water q.s.p.	100 ml.	pH: 7.5 $\pm$ 0.1	

5.6 BIBLIOGRAPHY

SOURCE CONSULTED

Chemical Abstracts from 1967 to September 1976 (Vol.12) from the five-year tables for 1967 to 1971 and by computer questioning beyond 1971.

We found nothing for methylene diisocyanate and methylene diamine and only 3 articles for toluylene diisocyanate or toluylene diamine.

The chemical oxygen demand from a residual water laden with TDI and TDA may pass from 34.000 ppm to 700 ppm by treatment with an amine (formalin), filtration of the supernatant and oxidation (Na Cl 10).

The diamines formed by hydrolysis of the diisocyanates are fairly stable. After 30 days at 20°, the concentration decreases 30 to 50% by conversion in polyurea.

The TDI gives 20 diamine for 85 of polyurea.

Waste waters from manufacture of TDA are not toxic for saporaphytic flora and infusoria when they contain 85 to 150 mg/1 of TDA, on the other hand nitrification is not impeded by 5 mg/1 of TDA.

Translator's note

Please note that page 32 of the original is entirely in English.

CERTIFICATE OF AUTHENTICITY

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